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54 PROCESS FOR PRODUCING MALEIMIDE COPOLYMER, AND THERMOPLASTIC RESIN PREPARED BY USING SAID COPOLYMER.

57 A process for producing maleimide copolymer, which comprises conducting suspension polymerization of a maleimide monomer and at least one monomer selected from the group consisting of an aromatic vinyl monomer, vinyl cyanide monomer, and methyl methacrylate monomer by using a calcium phosphate dispersing agent as a suspending and dispersing agent and dissolving a phosphate nonionic surfactant in the monomers. This process serves to stabilize the polymerization system and minimize adhesion of resulting polymer to the inside wall of a polymerization tank. A thermoplastic resin composition is also disclosed, which is prepared by blending the above-described maleimide copolymer with a specific rubber-modified graft copolymer. This resin composition has excellent heat stability upon high-temperature molding and resistance to coloration, heat and impact.

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SPECIFICATION

PROCESS FOR THE PREPARATION OF MALEIMIDE
COPOLYMERS AND THERMOPLASTIC RESIN COMPOSITION
5 USING SUCH COPOLYMERS

Technical Field

This invention relates to a suspension
polymerization process for the preparation of maleimide
10 copolymers having excellent thermal resistance and
thermal stability, which process brings about excellent
polymerization stability and causes almost no polymer
to adhere to the walls of the polymerization vessel, as
well as to a thermoplastic resin composition using
15 maleimide copolymers prepared by this process.

Prior Art

In recent years, the demand for improved
thermal resistance of materials for automobile parts has
20 increased. Especially for the manufacture of internal
trim parts such as dash board panels and the like, a
material having high thermal resistance and good mold-
ability is in urgent demand.

It is well known that maleimide polymers and
25 copolymers are materials having excellent thermal
resistance. However, since these polymers are very poor

in impact strength and moldability, they are usually blended with a rubber moldified polymer such as an ABS resin, AES resin and AAS resin in order to overcome such shortcomings. Nevertheless, even in maleimide resin compositions whose impact strength and moldability are improved by this means, there is still much room for improvement in impact strength and moldability when compared with common ABS resin, AES resin and AAS resin. In particular, an improvement in moldability is strongly desired. More specifically, in the field of current automotive industry, large-sized molding machines are in common use for molding and the material tends to stay at high temperature for a long period of time. Thus, it is desirable to develop a heat-resisting resin having excellent thermal stability and good moldability.

In synthesizing a copolymer containing a maleimide monomer as a constituent in order to improve its thermal resistance, it has been common practice to employ the emulsion polymerization or suspension polymerization technique. However, where a maleimide copolymer is synthesized according to the emulsion polymerization technique, the emulsifier used in the emulsion polymerization step remains in the resulting maleimide copolymer. Accordingly, it is known that, when the copolymer thus obtained is blended with ABS resin, AES resin or AAS resin, the residual emulsifier

undergoes thermal decomposition during high-temperature molding at 280°C or above, developing so-called silver streaks on the surfaces of molded articles or causing thermal discoloration.

5 On the other hand, where a maleimide copolymer is synthesized according to the suspension polymerization technique, the copolymer obtained by using a maleimide monomer has a high glass transition temperature (T_g) and, therefore, the polymerization must be carried out
10 at a high temperature in order to enhance the polymer yield. However, the system in which a hydrophilic high-molecular compound such as polyvinyl alcohol, a partial saponification product of polymethyl methacrylate or polyacrylamide is used as the suspension dispersant
15 during polymerization at a high temperature has the disadvantage that the thermal resistance of the dispersant itself is inadequate and, therefore, the dispersion stability is low. As a result, the suspension polymerization system is so unstable that it may
20 consolidate into a mass or, if not, the resulting beads may not be uniform in diameter and a large amount of polymer may adhere to the walls of the polymerization vessel. Moreover, even if the suspension polymerization using a hydrophilic high-molecular compound is completed
25 satisfactorily, the hydrophilic high-molecular compound thermally decomposes during high-temperature molding.

For these reasons, it is disadvantageous to use such a hydrophilic high-molecular compound as the suspension dispersant in the synthesis of a maleimide copolymer.

Accordingly, in the case of suspension
5 polymerization, calcium phosphate compounds, calcium carbonate compounds, kaolin, talc and the like have been commonly used as dispersants. Moreover, where calcium phosphate compounds are used as dispersants, fatty acid soaps such as sodium oleate and sodium
10 stearate, anionic surface-active agents such as sodium dodecylsulfonate and sodium dodecylbenzenesulfonate, and nonionic surface-active agents such as polyoxyethylene monostearyl ester and polyoxyethylene monooleyl ester, have been commonly used as dispersing
15 agents. However, the use of this kind of emulsifier has been found to pose a problem in that a considerable amount of polymer adheres to the inner walls of the polymerization vessel and causes a reduction in workability and productivity.

20 In view of these circumstances, the present inventors conducted intensive studies and have found that, in a suspension polymerization process for the preparation of maleimide copolymers, all of the above-described disadvantages can be overcome by carrying
25 out the suspension polymerization while using a calcium phosphate dispersant as the suspension dispersant and

while allowing a specific amount of a phosphoric ester type nonionic surface-active agent to be dissolved in the monomers. Moreover, they also found that a resin composition having excellent thermal resistance, thermal stability and impact resistance can be obtained by blending a maleimide copolymer prepared by this suspension polymerization process with a specific graft copolymer. The present invention was completed on the basis of these discoveries.

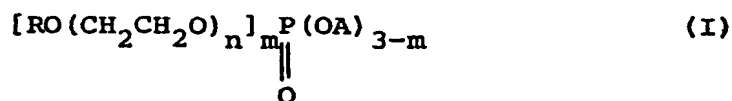
Disclosure of the Invention

It is an object of the present invention to provide a suspension polymerization process for the preparation of maleimide copolymers which process brings about excellent polymerization stability and causes almost no polymer to adhere to the walls of the polymerization vessel.

It is another object of the present invention to provide a thermoplastic resin composition formed by blending a maleimide copolymer prepared by this process with a specific graft copolymer and characterized by excellent thermal resistance, thermal stability and impact resistance.

According to the present invention, there is provided a process for the preparation of maleimide copolymers by suspension polymerization of 50 to 95% by

weight of at least one monomer selected from the group consisting of aromatic vinyl monomers, vinyl cyanide monomers and methyl methacrylate monomer, 5 to 50% by weight of a maleimide monomer, and 0 to 30% by weight of a monomer copolymerizable therewith, provided that the total amount of said monomers is 100% by weight, said process being characterized by carrying out said suspension polymerization while using a calcium phosphate dispersant as the suspension dispersant and while allowing a phosphoric ester type nonionic surface-active agent of the general formula



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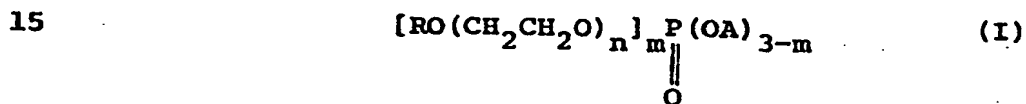
where R is an alkyl or aralkyl group of 8 to 30 carbon atoms, A is a hydrogen atom or a metal capable of forming a water-soluble salt, m is an integer of 1 to 3, and n is an integer of 5 to 50, to be dissolved in said monomers in an amount of 0.0001 to 0.5 part by weight per 100 parts by weight of the mixture of said monomers.

According to the present invention, there is also provided a thermoplastic resin composition comprising

25

[A] 40 to 90% by weight of a maleimide copolymer

prepared from 50 to 95% by weight of at least one monomer selected from the group consisting of aromatic vinyl monomers, vinyl cyanide monomers and methyl methacrylate monomer, 5 to 50% by weight of a maleimide monomer, and 0 to 30% by weight of a monomer copolymerizable therewith, provided that the total amount of said monomers is 100% by weight, said copolymer having been obtained by subjecting said monomers to suspension polymerization while using a calcium phosphate dispersant as the suspension dispersant and while allowing a phosphoric ester type nonionic surface-active agent of the general formula



where R is an alkyl or aralkyl group of 8 to 30 carbon atoms, A is a hydrogen atom or a metal capable of forming a water-soluble salt, m is an integer of 1 to 3, and n is an integer of 5 to 50, to be dissolved in said monomers in an amount of 0.0001 to 0.5 part by weight per 100 parts by weight of the mixture of said monomers; and

[B] 10 to 60% by weight of a graft copolymer formed by subjecting at least one monomer selected from

the group consisting of aromatic vinyl monomers, vinyl cyanide monomers and methyl methacrylate monomer to graft polymerization on a rubber polymer;

- 5 the total amount of said copolymers [A] and [B] being 100% by weight.

Best Mode for Carrying Out the Invention

- 10 The aromatic vinyl monomers which can be used as starting materials in the polymerization reaction for preparing a maleimide copolymer include, for example, styrene, α -methylstyrene, p-methylstyrene, tert-butylstyrene, chlorostyrene, bromostyrene and the like. The vinyl cyanide monomers which can be used
- 15 for the same purpose include, for example, acrylonitrile, methacrylonitrile and the like. Aromatic vinyl monomers, vinyl cyanide monomers and methyl methacrylate monomer may be used alone or in combination, and the total amount of such monomers may be 50 to 95% by weight.
- 20 If the total amount is less than 50% by weight, the resulting copolymer will have high melt viscosity and tend to be inconvenient for molding purposes. If the total amount is greater than 95% by weight, an improvement in thermal resistance will tend to be almost
- 25 impossible to achieve.

The maleimide monomers which can be used

with the aforesaid monomers include, for example, maleimide, N-methylmaleimide, N-ethylmaleimide, N-phenylmaleimide, N-halophenylmaleimides, N-alkyl-phenylmaleimides, N-cyclohexylmaleimide and the like.

- 5 These maleimide monomers may be used alone or in an admixture of two or more, and the amount of maleimide monomer used may be 5 to 50% by weight.

- The monomers which are copolymerizable with aromatic vinyl monomers, vinyl cyanide monomers, methyl methacrylate and maleimide monomers include, for example, vinyl acetate, fumaronitrile, isopropyl fumarate, acenaphthylene and the like. These copolymerizable monomers are optional components, and need not necessarily be used as starting materials in the practice of the present invention. They may be used in an amount of 0 to 30% by weight.

- In the present invention, the suspension polymerization is carried out by using a calcium phosphate compound as the suspension dispersant.
- 20 Specific examples of useful calcium phosphate dispersants include calcium tertiary phosphate, calcium secondary phosphate, calcium hydrogen phosphate, hydroxyapatite and the like. These calcium phosphate dispersants may be used alone or in an admixture of two or more. The amount of calcium phosphate dispersant added may usually
- 25 be 0.1 to 3 parts by weight, preferably 0.3 to 2 parts

by weight, per 100 parts by weight of the mixture of the aforesaid monomers. If the amount is less than 0.1 part by weight, it may be difficult to establish a stable suspension system, while if it is greater than 3 parts by weight, the dispersant will be incorporated into the polymer and cause deterioration of its quality.

Also in the present invention, a phosphoric ester type nonionic surface-active agent of the aforesaid formula (I) is used as a dispersing agent. As a result of investigation into a variety of surface-active agents, the present inventors have found that such a phosphoric ester type nonionic surface-active agent can act not only as a suspension dispersing agent in the preparation of a maleimide copolymer by suspension polymerization, but also as a thermal stabilizer in molding the maleimide copolymer at high temperature. This is the reason why such a surface-active agent is used in the suspension polymerization reaction of the present invention.

In the above formula (I) representing the structure of a phosphoric ester type nonionic surface-active agent, R represents an alkyl or aralkyl group of 8 to 30 carbon atoms. Specific examples of the alkyl group of 8 to 30 carbon atoms include lauryl, stearyl and the like, and specific examples of the

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aralkyl group of 8 to 30 carbon atoms include
nonylphenyl and the like. On the other hand, A may
represent a metal capable of forming a water-soluble
salt and specific examples of the metal include sodium,
5 potassium and the like.

Specific examples of this phosphoric ester
type nonionic surface-active agent include Gafac
GB520, Gafac RS610, Gafac RS710, Gafac RE410, Gafac
RE610 and Gafac RE960, all of which are commercial
10 products of Toho Chemicals Co., Ltd.

These surface-active agents may be used
alone or in an admixture of two or more, and they may
also be used in combination of other anionic surface-
active agents. Prior to the suspension polymerization,
15 the phosphoric ester type nonionic surface-active
agent may usually be dissolved in the aforesaid monomers
in an amount of 0.0001 to 0.5 part by weight, prefer-
ably 0.001 to 0.1 part by weight, per 100 parts by
weight of the mixture of the aforesaid monomers. If
20 the amount is less than 0.0001 part by weight, the
surface-active agent may fail to be satisfactorily
effective in preventing the polymer from adhering to
the walls of the polymerization vessel, and if it is
greater than 0.5 part by weight, the surface-active
25 agent will exert an adverse effect on the stability
of the suspension polymerization and cause the system

to consolidate into a mass.

Using the aforesaid monomers as starting materials, the suspension polymerization reaction for the preparation of a maleimide copolymer in accordance with the present invention may be carried out, for example, in the following manner: The aforesaid monomers, dispersant and surface-active agent are charged into a reactor and an sufficient amount of a radical polymerization initiator is added thereto. This mixture is usually heated at a temperature of 50 to 130°C for 2 to 8 hours to effect the polymerization reaction. After completion of the reaction, the resulting bead polymer is dehydrated, washed and then dried to obtain the desired maleimide copolymer [A]. This copolymer [A] has the properties of high thermal resistance and undergoing little discoloration or thermal decomposition during high-temperature molding.

On the other hand, the graft copolymer [B] used in the present invention is a polymer obtained by subjecting at least one monomer selected from the group consisting of aromatic vinyl monomers, vinyl cyanid monomers and methyl methacrylate to graft polymerization on a rubber polymer.

The rubber polymers which can be used for this purpose include, for example, diene rubbers

composed mainly of a diene monomer (such as polybutadiene, polyisoprene and butadiene-styrene copolymer), acrylic rubbers composed mainly of an acrylic ester (such as acrylic rubber composed mainly of butyl acrylate) and ethylene-propylene-diene (EPDM) rubber, but are not limited thereto. These rubber polymers may be used alone or in an admixture of two or more.

Useful aromatic vinyl monomers include, for example, styrene, α -methylstyrene, p-methylstyrene, tert-butylstyrene, chlorostyrene, bromostyrene and the like. They may be used alone or in an admixture of two or more.

Useful vinyl cyanide monomers include, for example, acrylonitrile, methacrylonitrile and the like. They may be used alone or in an admixture of two or more.

In the formation of the graft copolymer, the rubber polymer may be used in an amount of 20 to 70 parts by weight, while the aromatic vinyl monomer(s), vinyl cyanid monomer(s) and/or methyl methacrylate monomer may be used in the total amount of 80 to 30 parts by weight. If the amount of rubber polymer used is less than 20 parts by weight, an adequate degree of impact resistance may not be exhibited. In such a case, a larger amount of graft copolymer [B] must be blended with copolymer [A], which tends to cause a

reduction in thermal resistance. If the amount of rubber polymer used is greater than 70 parts by weight, it will be difficult to obtain a copolymer having a high degree of impact resistance.

5 The thermoplastic resin composition of the present invention comprises 40 to 90% by weight of the aforesaid maleimide copolymer [A] and 10 to 60% by weight of the aforesaid graft copolymer [B], provided that the total amount of both copolymers is 100% by
10 weight. If the proportions of both copolymers are outside the above-described range, it will be difficult to obtain a thermoplastic resin composition having excellent thermal resistance, thermal stability and impact resistance. Moreover, the molded articles
15 obtained by using this resin composition will have low gloss and, in addition, will tend to develop silver streaks and hence have a poor surface appearance.

 The thermoplastic resin composition of the present invention can be formed, for example, by mixing
20 dried powders of the aforesaid copolymers [A] and [B] in a Henschel mixer, kneading the mixture in a vented extruder, Banbury mixer, roll mill or the like, and then pelletizing it. Thus, there is obtained a thermoplastic resin composition characterized by excellent
25 thermal resistance, low thermal decomposability, little deterioration by discoloration during molding, excellent

impact resistance and good flowability.

The present invention is further illustrated by the following examples. In these examples, all parts are by weight.

5 In these examples, the thermal decomposability and thermal discoloration of a maleimide copolymer alone were evaluated according to the following procedures.

10 Procedure for the evaluation of thermal decomposability

 Using a thermogravimetric analysis (Model TGA-30; manufactured by Shimadzu Corporation), a polymer sample was heated at a rate of 10°C/min in an atmosphere of 30 ml/min of nitrogen gas and its weight loss was
15 measured. The temperature at which the polymer sample lost 5% by weight of its original weight was taken as a measure of thermal decomposability.

Procedure for the evaluation of thermal discoloration

20 Using a 1-ounce vertical injection molding machine, the copolymer was molded under the following conditions.

 Mold configuration: Flat plate having a size of
 50 x 80 x 3^t mm
25 Mold temperature: 60°C
 Cylinder temperature: 280°C (preset)

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Injection speed: 10 seconds

Molding cycle: 60 seconds

The thermal discoloration of the molded plate was evaluated according to the following criteria.

5 Thermal discoloration:

- No appreciable change was noted by visual inspection.
- Δ A slight degree of discoloration was noted by visual inspection.
- 10 X A marked degree of discoloration was noted by visual inspection.

The thermal decomposability and thermal discoloration of a resin composition comprising a maleimide copolymer and a graft copolymer were evaluated according to the following procedures.

Procedures for the evaluation of thermal decomposability and thermal discoloration

20 Using a 1-ounce vertical injection molding machine, the resin composition was molded under the following conditions.

- Mold configuration: Flat plate having a size of 50 x 80 x 3^t mm
- 25 Mold temperature: 60°C
- Cylinder temperature: 290°C (for the evaluation of thermal decomposability)

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280°C (for the evaluation of
thermal discoloration)

Injection speed: 10 seconds

Molding cycle: 60 seconds

5 The surface appearance of the plate molded at
a cylinder temperature of 290°C was examined for the
development of silver streaks owing to thermal decompo-
sition. On the basis of the number of silver streaks,
the thermal decomposability of the resin composition
10 was evaluated according to the following criteria.

Thermal decomposability:

○ No silver streaks were observed.

△ Some silver streaks were observed.

X A large number of silver streaks were observed.

15 XX An immense number of silver streaks were observed.

Thermal discoloration:

 The degree of yellowness (YI value according
to JIS K-7103) of the plate molded at a cylinder
temperature of 280°C was measured by means of a color
20 computer (manufactured by Suga Testing Machine Co.,
Ltd.).

Example 1

Preparation of maleimide copolymer [A]

25 The following materials were charged into a
3-liter autoclave (made of SUS #32):

Monomer phase:

	Acrylonitrile (AN)	20	parts
	Styrene (ST)	70	parts
	N-Phenylmaleimide (P-MI)	10	parts
5	Azobisisobutyronitrile (AIBN)	0.1	part
	tert-Butyl perbenzoate (t-BPB)	0.1	part
	tert-Dodecyl mercaptan (t-DM)	0.3	part
	Gafac [®] GB520 [of formula (I) in which R = lauryl, A = sodium, m = 2, n = 6]	0.003	part

10 Aqueous phase:

	Distilled water	100	parts
	Calcium tertiary phosphate (TCP)	0.5	part

Specifically, after the 3-liter autoclave
 15 was thoroughly purged with N₂, the aqueous-phase
 components were first charged thereinto. Separately,
 the monomer-phase components were mixed well to form
 a solution. This solution was charged into the auto-
 20 clave and stirring was started. The internal tempera-
 ture was raised to 80°C and held at that level for 3
 hours to effect the reaction. Thereafter, the internal
 temperature was raised to 120°C and the polymerization
 was continued for an additional 2 hours. Then, the
 25 autoclave were observed after completion of the poly-
 merization, almost no polymer was found to be attached
 thereto.

The resulting bead polymer was dehydrated with a centrifugal dehydrator, treated with 1N dilute sulfuric acid to dissolve and remove the TCP, washed well and then dried in a hot-air dryer at 90°C for 5 48 hours to obtain spherical beads. The average diameter of the beads was 180 μ m. The glass transition temperature (T_g) of the copolymer thus obtained was 125°C.

Then, the above copolymer was pelletized at 10 250°C by means of a 40 mm ϕ extruder. Part of the pellets thus obtained were used to evaluate the thermal decomposability of the copolymer. Moreover, a flat plate having a size of 50 x 80 x 3^t mm was formed of these pellets by means of a 1-ounce vertical injection 15 molding machine and used to evaluate its thermal discoloration. The results of evaluation are shown in Table 1.

Preparation of graft copolymer [B]

20 The following materials were charged into a 5-liter reactor made of glass.

25	Polybutadiene latex Ethylenediaminetetraacetic acid disodium salt Ferrous sulfate	50 parts (as solid content) 0.01 part 0.003 part
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Sulfosuccinate	0.3	part
Distilled water	150	parts
Potassium rosinate	1	part
Potassium hydroxide	0.01	part

5 The reactor was purged with N₂ and then heated
to 65°C. Thereafter, a mixture of 15 parts of acrylo-
nitrile, 35 parts of styrene, 0.3 part of cumene
hydroperoxide (CHP) and 0.3 part of tert-dodecyl
mercaptan (t-DM) was added dropwise to the reactor
10 over a period of 3 hours. After completion of the
addition, an additional 0.1 part of CHP was supplemented.
Then, the reaction mixture was heated to 75°C and held
at that temperature for 2 hours to complete the polymer-
ization. To the resulting ABS-grafted latex was added
15 0.1 part of Antage W-400 (trade name, an antioxidant
commercially available from Sumitomo Chemical Co., Ltd.).
The latex was coagulated with 1% dilute sulfuric acid,
dehydrated with a centrifugal dehydrator, washed and
then dried to obtain a white powder.

20

Preparation of a resin composition

 The copolymers [A] and [B] prepared according
to the above-described procedures were mixed in a
proportion of 55 parts to 45 parts, and 0.3 part of
25 magnesium stearate, 0.1 part of tris(nonylphenyl)
phosphite and 0.2 part of Antage W-400 were added

thereto. This mixture was intimately blended in a tumbler and then pelletized at 250°C by means of a 40 mm ϕ extruder. Flat plates having a size of 80 x 50 x 3^t mm were formed of the resulting pellets by means of a 1-ounce vertical injection molding machine and used to evaluate the thermal discoloration, thermal decomposability and other properties of the resin composition. The results of evaluation are shown in Table 2.

Example 2

Preparation of maleimide copolymer [A]

The following materials were charged into a 3-liter autoclave.

Monomer phase:

AN	16	parts
ST	64	parts
P-MI	20	parts
AIBN	0.1	part
t-BPB	0.1	part
t-DM	0.3	part
Gafac [®] GB520	0.003	part

Aqueous phase:

Distilled water	100	parts
TCP	0.5	part

The above materials were polymerized in the same manner as described in Example 1. The beads thus obtained were slightly yellowish, spherical particles and their average diameter was 200 μ m. A
5 very small amount of polymer was found to be attached to the inner walls of the autoclave. The Tg of the copolymer was 135°C.

Then, the above beads were used to evaluate the copolymer in the same manner as described in
10 Example 1. The results of evaluation are shown in Table 1.

Preparation of a resin composition

A blend of the beads obtained in the above-described manner and the graft copolymer obtained in
15 Example 1 was pelletized and molded in the same manner as described in Example 1, and various properties thereof were evaluated. The results of evaluation are shown in Table 2.

20

Example 3

Preparation of maleimide copolymer [A]

Polymerization was carried out in the same manner as described in Example 1, except that Gafac[®]
25 GB520 was replaced by Gafac[®] RE610 [of formula (I) in which R = nonylphenyl, A = hydrogen, m = 2 and n = 6].

The beads thus obtained were spherical particles and had an even particle size distribution with an average diameter of 190 μ m. The Tg of the copolymer was 124°C. After completion of the polymerization, a very small amount of polymer was found to be attached to the inner walls of the autoclave.

Then, the above beads were used to evaluate the copolymer itself in the same manner as described in Example 1. The results of evaluation are shown in Table 1.

Preparation of a resin composition

A blend of the beads obtained in the above-described manner and the graft copolymer obtained in Example 1 was pelletized and molded in the same manner as described in Example 1, and various properties thereof were evaluated. The results of evaluation are shown in Table 2.

20 Example 4

Preparation of maleimide copolymer [A]

The following materials were charged into a 3-liter autoclave.

Monomer phase:

25	AN	12.5 parts
	ST	57.5 parts

P-MI	30	parts
AIBN	0.1	part
t-BPB	0.1	part
Gafac [®] GB520	0.02	part

5

Aqueous phase:

Distilled water	100	parts
TCP	0.5	part

Specifically, the aqueous-phase components
10 were first charged into the 3-liter autoclave, which
was thoroughly purged with N₂. Then, the monomer-
phase components were charged thereinto and stirring
was started. The internal temperature was raised to
80°C and held at that level for 3 hours. Thereafter,
15 the internal temperature was raised to 130°C and held
at that level for 2 hours. The resulting beads were
dehydrated with a centrifugal dehydrator and treated
with 1N dilute sulfuric acid to dissolve the TCP
thoroughly. After dehydration and water washing were
20 repeated twice, they were dried in a hot-air dryer at
100°C for 24 hours. The beads thus obtained were
perfectly spherical particles and had an average
diameter of 250 μm. The T_g of the copolymer was 144°C.
Moreover, a very small amount of polymer was found to
25 be attached to the inner walls of the autoclave.

Then, the above beads were used to evaluate

the copolymer itself in the same manner as described in Example 1. The results of evaluation are shown in Table 1.

5 Preparation of a resin composition

 A blend of the beads obtained in the above-described manner and the graft copolymer obtained in Example 1 was pelletized and molded in the same manner as described in Example 1, and various properties
10 thereof were evaluated. The results of evaluation are shown in Table 2.

Example 5

Preparation of maleimide copolymer [A]

15 The following materials were charged into a 3-liter autoclave.

Monomer phase:

	AN	5	parts
	ST	55	parts
20	Methyl methacrylate (MMA)	20	parts
	P-MI	20	parts
	AIBN	0.1	part
	t-BPB	0.1	part
	t-DM	0.3	part
25	Gafac [®] RE610	0.01	part

Aqueous phase:

Distilled water	100	parts
TCP	0.5	part

The above materials were polymerized in the same manner as described in Example 1. After completion of the polymerization, a very small amount of polymer was found to be attached to the inner walls of the autoclave. After the resulting beads were thoroughly washed with 1N dilute sulfuric acid, dehydration and water washing were repeated twice. Then, they were dried at 100°C for 24 hours. The beads thus obtained were perfectly spherical particles and had an average diameter of 255 μ m. The Tg of the copolymer was 140°C.

Then, the above beads were used to evaluate the copolymer itself in the same manner as described in Example 1. The results of evaluation are shown in Table 1.

Preparation of a resin composition

A blend of the beads obtained in the above-described manner and the graft copolymer obtained in Example 1 was pelletized and molded in the same manner as described in Example 1, and various properties thereof were evaluated. The results of evaluation are shown in Table 2.

Example 6Preparation of maleimide copolymer [A]

The following materials were charged into a 3-liter autoclave.

5

Monomer phase:

	AN	20	parts
	ST	20	parts
	α -Methylstyrene (α MS)	35	parts
10	P-MI	25	parts
	AIBN	0.1	part
	t-BPB	0.2	part
	t-DM	0.3	part
	Gafac [®] GB520	0.01	part

15

Aqueous phase:

	Distilled water	100	parts
	TCP	0.5	part

The above materials were polymerized in the same manner as described in Example 1. After completion of the polymerization, a very small amount of polymer was found to be attached to the inner walls of the autoclave. After the resulting beads were thoroughly washed with 1N dilute sulfuric acid, dehydration and water washing were repeated twice. Then, they were dried at 100°C for 24 hours. The beads thus obtained were perfectly spherical particles

and had an average diameter of 220 μ m. The Tg of the copolymer was 150°C.

Then, the above beads were used to evaluate the copolymer itself in the same manner as described in Example 1. The results of evaluation are shown in Table 1.

Preparation of a resin composition

A blend of the beads obtained in the above-described manner and the graft copolymer obtained in Example 1 was pelletized and molded in the same manner as described in Example 1, and various properties thereof were evaluated. The results of evaluation are shown in Table 2.

Comparative Example 1

Preparation of a maleimide copolymer

The following materials were charged into a 3-liter autoclave.

20

Monomer phase:

AN	20	parts
ST	70	parts
P-MI	10	parts
AIBN	0.1	part
t-BPB	0.1	part
t-DM	0.3	part

25

Aqueous phase:

Distilled water	120 parts
Polyvinyl alcohol (PVA) [having a degree of polymerization of 1500]	0.5 part

5 The above materials were polymerized in the
autoclave in the same manner as described in Example 1.
Then, beads were obtained by dehydration, water washing
and drying. The beads thus obtained were not uniform
in diameter (with an average diameter of 350 μ m) and
10 included a considerable number of bubble-containing
particles and abnormally large particles, suggesting
that the suspension polymerization system had been
unstable. Moreover, a large amount of polymer was
found to be attached to the inner walls of the auto-
15 clave. The Tg of the copolymer thus obtained was
124°C.

Then, the above beads were used to evaluate
the copolymer itself in the same manner as described
in Example 1. The results of evaluation are shown in
20 Table 1.

Preparation of a resin composition

A blend of the beads obtained in the above-
described manner and the graft copolymer obtained in
25 Example 1 was pelletized and molded in the same manner
as described in Example 1, and various properties

thereof were evaluated. The results of evaluation are shown in Table 2.

Comparative Example 2

5 Preparation of a maleimide copolymer

Polymerization was carried out in the same manner as described in Comparative Example 1, except that the PVA used as the suspension dispersant was replaced by 0.5 part of a partial saponification product (or KOH-treated product) of PMMA (PMMA-derived dispersant). The beads thus obtained were accompanied by a large amount of floating polymer and had an average diameter of as large as 430 μm , suggesting that the polymerization system had been unstable.

10

15 Moreover, a large amount of polymer was found to be attached to the inner walls of the autoclave. The T_g of the copolymer thus obtained was 125°C.

Then, the above beads were used to evaluate the copolymer itself in the same manner as described in Example 1. The results of evaluation are shown in Table 1.

20

Preparation of a resin composition

A blend of the beads obtained in the above-described manner and the graft copolymer obtained in Example 1 was pelletized and molded in the same

25

manner as described in Example 1, and various properties thereof were evaluated. The results of evaluation are shown in Table 2.

5 Comparative Example 3

Preparation of a maleimide copolymer

Polymerization was carried out in the same manner as described in Example 2, except that 0.01 part of potassium oleate, an anionic surface-active agent, was used in place of 0.01 part of Gafac[®] GB-520. After completion of the polymerization, a large amount of copolymer was found to be attached as a film to the inner walls of the autoclave. The beads thus obtained had a wide size distribution with an average diameter of 350 μ m and included many larger particles. The Tg of this copolymer was 136°C.

Then, the above beads were used to evaluate the copolymer itself in the same manner as described in Example 1. The results of evaluation are shown in Table 1.

Preparation of a resin composition

A blend of the beads obtained in the above-described manner and the graft copolymer obtained in Example 1 was pelletized and molded in the same manner as described in Example 1, and various properties

thereof were evaluated. The results of evaluation are shown in Table 1.

Comparative Example 4

5 Preparation of a maleimide copolymer

The following materials were charged into a 5-liter reactor made of glass.

	Distilled water	200	parts
	Sodium lauryl sulfate	3	parts
10	Acid sodium sulfite	1	part
	Potassium persulfate	0.5	part

After the mixture was heated to 60°C, a solution composed of 20 parts of AN, 70 parts of ST and 10 parts of P-MI was added dropwise thereto over a period of 3 hours. After completion of the addition, an additional 0.1 part of potassium persulfate was supplemented. Then, the reaction system was heated to 70°C and held at that temperature for 2 hours to complete the polymerization. The monomer conversion was 93%.

The resulting latex was coagulated with magnesium sulfate, washed, dehydrated and dried to obtain a white copolymer powder. The T_g of this copolymer was 135°C.

25 Then, the above white copolymer powder was used to evaluate the copolymer itself in the same manner

as described in Example 1. The results of evaluation are shown in Table 1.

Preparation of a resin composition

5 A blend of the copolymer powder obtained in the above-described manner and the graft copolymer obtained in Example 1 was pelletized and molded in the same manner as described in Example 1, and various properties thereof were evaluated. The results of
10 evaluation are shown in Table 2.

Table 1

	Monomers charged (parts)						Suspension dispersants (parts)			Dispersing agents (parts)	
							TCP	PVA	PMMA-derived	Phosphoric ester type surfactant	Potassium oleate
	AN	ST	MMA	P-MI	αMS						
Example 1	20	70	-	10	-	0.5	-	-	GB-520 0.003	-	
" 2	16	64	-	20	-	0.5	-	-	GB-520 0.01	-	
" 3	20	70	-	10	-	0.5	-	-	RE-610 0.003	-	
" 4	12.5	57.5	-	30	-	0.5	-	-	GB-520 0.02	-	
" 5	5	55	20	20	-	0.5	-	-	RE-610 0.01	-	
" 6	20	20	-	25	35	0.5	-	-	GB-520 0.02	-	
Comparative Example 1	20	70	-	10	-	-	0.5	-	-	-	
" 2	20	70	-	10	-	-	-	0.5	-	-	
" 3	16	64	-	20	-	0.5	-	-	-	0.01	
" 4	20	70	-	10	-	-	-	-	-	-	

* Indications of adhesion to the polymerization vessel - to be cont'd -

○ : Very little polymer was found to be attached to the inner walls of the polymerization vessel.

x : A large amount of polymer was found to be attached to the inner walls of the polymerization vessel.

Table 1 (Cont'd)

Adhesion to polymer- ization vessel*	Thermal decompos- ability (°C)	Thermal discolor- ation	Tg (°C)
○	380	○	125
○	371	○	135
○	380	○	124
○	365	○	144
○	360	○	140
○	360	○	150
x	351	Δ	124
x	352	Δ	125
x	351	○	136
○	340	x	135

Table 2

	Thermal decompos- ability (290°C)	Thermal discolor- ation (280°C) [YI value]	Notched Izod impact strength (kg·cm/cm ²) [ASTM D-256]	Melt flow index (g/10 min) [ASTM D-1238]	Rockwell hardness (R scale) [ASTM D-785]	Vicat softening temperature (°C) [ISO-R306]
Example 1	○	31	16.4	11	102	108
" 2	○	30	9	7.2	103	112
" 3	○	29	16.2	12	102	107
" 4	○	33	5	4	105	122
" 5	○	28	4	6.2	104	115
" 6	○	30	4	3	105	125
Comparative Example 1	X	44	15.5	12	102	105
" 2	X	41	16	11	101	104
" 3	Δ	38	8	7	104	113
" 4	XX	51	17	7.4	103	113

Examples 7 to 12

5 Resin composition were prepared by blending the graft copolymer obtained in Example 1 with each of the maleimide copolymers obtained in Examples 1, 2 and 4 in each of the proportions shown in Table 3. These resin compositions were pelletized and molded in the same manner as described in Example 1, and various properties thereof were evaluated. The results of evaluation are shown in Table 3.

Table 3

	Formulation of resin composition (weight ratio)	Thermal decompos- ability (290°C)	Thermal discolor- ation (280°C) [YI value]	Notched Izod impact strength (kg·cm/cm ²) [ASTM D-256]
Example 7	Graft copolymer/male- imide copolymer of Example 1 = 50/50	○	33	19.5
" 8	Graft copolymer/male- imide copolymer of Example 1 = 40/60	○	29	12
" 9	Graft copolymer/male- imide copolymer of Example 2 = 50/50	○	31	11
" 10	Graft copolymer/male- imide copolymer of Example 2 = 40/60	○	28	6
" 11	Graft copolymer/male- imide copolymer of Example 4 = 50/50	○	35	6.7
" 12	Graft copolymer/male- imide copolymer of Example 4 = 40/60	○	31	4

- to be cont'd -

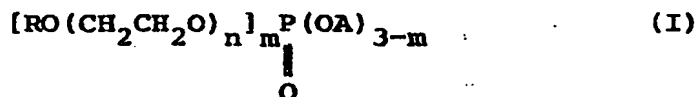
Table 3 (Cont'd)

Melt flow index (g/10 min) [ASTM D-1238]	Rockwell hardness (R scale) [ASTM D-785]	Vicat softening temperature (°C) [ISO-R306]
9.2	100	102
14	106	114
6	101	108
9.1	107	116
3	102	118
5.2	108	128

The suspension polymerization process of the present invention brings about excellent stability of the polymerization system and causes almost no polymer to adhere to the inner walls of the polymerization vessel. Moreover, the process of the present invention can provide a maleimide copolymer which does not undergo discoloration or thermal decomposition during high-temperature molding. Furthermore, the resin composition of the present invention, formed by blending this maleimide copolymer with a specific rubber-modified graft copolymer, has not only excellent thermal stability and resistance to discoloration during high-temperature molding, but also very excellent thermal resistance and impact resistance.

CLAIMS

1. A process for the preparation of maleimide copolymers by suspension polymerization of 50 to 95% by weight of at least one monomer selected from the group consisting of aromatic vinyl monomers, vinyl cyanide monomers and methyl methacrylate monomer, 5 to 50% by weight of a maleimide monomer, and 0 to 30% by weight of a monomer copolymerizable therewith, provided that said process being characterized by carrying out said suspension polymerization while using a calcium phosphate dispersant as the suspension dispersant and while allowing a phosphoric ester type nonionic surface-active agent of the general formula



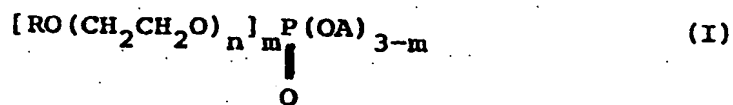
where R is an alkyl or aralkyl group of 8 to 30 carbon atoms, A is a hydrogen atom or a metal capable of forming a water-soluble salt, m is an integer of 1 to 3, and n is an integer of 5 to 50, to be dissolved in said monomers in an amount of 0.0001 to 0.5 part by weight per 100 parts by weight of the mixture of said monomers.

2. A process as claimed in claim 1 wherein said maleimide monomer is at least one member selected from the group consisting of maleimide, N-methylmaleimide, N-ethylmaleimide, N-phenylmaleimide, N-halophenyl-
5 maleimides, N-alkylphenylmaleimides and N-cyclohexylmaleimide.

3. A process as claimed in claim 1 wherein said calcium phosphate dispersant is at least one member
10 selected from the group consisting of calcium tertiary phosphate, calcium secondary phosphate, calcium hydrogen phosphate and hydroxyapatite.

4. A thermoplastic resin composition comprising
15 [A] 40 to 90% by weight of a maleimide copolymer prepared from 50 to 95% by weight of at least one monomer selected from the group consisting of aromatic vinyl monomers, vinyl cyanide monomers and methyl methacrylate monomer, 5 to 50% by weight
20 of a maleimide monomer, and 0 to 30% by weight of a monomer copolymerizable therewith, provided that the total amount of said monomers is 100% by weight, said copolymer having been obtained by
25 subjecting said monomers to suspension polymerization while using a calcium phosphate dispersant as the suspension dispersant and while allowing a

phosphoric ester type nonionic surface-active
agent of the general formula



where R is an alkyl or aralkyl group of 8 to 30
carbon atoms, A is a hydrogen atom or a metal
capable of forming a water-soluble salt, m is an
integer of 1 to 3, and n is an integer of 5 to 50,
to be dissolved in said monomers in an amount of
0.0001 to 0.5 part by weight per 100 parts by
weight of the mixture of said monomers; and
[B] 10 to 60% by weight of a graft copolymer formed
by subjecting at least one monomer selected from
the group consisting of aromatic vinyl monomers,
vinyl cyanide monomers and methyl methacrylate
monomer to graft polymerization on a rubber polymer;
the total amount of said copolymers [A] and [B] being
100% by weight.

5. A thermoplastic resin composition as claimed
in claim 4 wherein said maleimide monomer is at least
one member selected from the group consisting of
maleimide, N-methylmaleimide, N-ethylmaleimide, N-
phenylmaleimide, N-halophenylmaleimides, N-alkylphenyl-
maleimides and N-cyclohexylmaleimide.

6. A thermoplastic resin composition as claimed in claim 4 wherein said calcium phosphate dispersant is at least one member selected from the group consisting of calcium tertiary phosphate, calcium
5 secondary phosphate, calcium hydrogen phosphate and hydroxyapatite.

7. A thermoplastic resin composition as claimed in claim 4 wherein said rubber polymer is at least one
10 member selected from the group consisting of diene rubbers composed mainly of a diene monomer, acrylic rubbers composed mainly of an acrylic ester, and ethylene-propylene-diene rubber.

15 8. A thermoplastic resin composition as claimed in claim 4 wherein said graft copolymer [B] is formed by subjecting 80 to 30 parts by weight of at least one monomer selected from the group consisting of aromatic vinyl monomers, vinyl cyanide monomers and methyl
20 methacrylate monomer to graft polymerization on 20 to 70 parts by weight of a rubber polymer.

INTERNATIONAL SEARCH REPORT

International Application No.

0208790
PCT/JP86/08017

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ²		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. ⁴ C08F2/18, C08F212/04, C08L33/14, C08L35/06, C08L51/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁵		
Classification System	Classification Symbols	
IPC	C08F2/18, C08F212/04, 06, 08, C08F222/40, C08L33/14, C08L35/06 C08L51/04	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹¹		
Category ⁷	Citation of Document, ¹² with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	JP, A, 49-83785 (Tokuyama Sekisui Kogyo Kabushiki Kaisha) 12 August 1974 (12. 08. 74) (Family: none)	1-3
Y	JP, A, 54-95689 (Mitsubishi Rayon Co., Ltd.) 28 July 1979 (28. 07. 79) (Family: none)	1-3
Y	JP, A, 57-125242 (Denki Kagaku Kogyo Kabushiki Kaisha) 4 August 1982 (04. 08. 82) & US, A, 4,404,322	4-8
Y	JP, A, 57-167341 (Asahi-Dow Limited) 15 October 1982 (15. 10. 82) (Family: none)	4-8
Y	JP, A, 58-129043 (Toray Industries, Inc.) 1 August 1983 (01. 08. 83) (Family: none)	4-8
Y	JP, A, 58-206657 (Denki Kagaku Kogyo Kabushiki Kaisha) 1 December 1983 (01. 12. 83) (Family: none)	4-8
<p>¹³ Special categories of cited documents: ¹⁴</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
March 28, 1986 (28. 03. 86)	April 14, 1986 (14. 04. 86)	
International Searching Authority ³	Signature of Authorized Officer ¹⁹	
Japanese Patent Office		

0208790

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, A, 59-184243 (Toray Industries, Inc.) 19 October 1984 (19. 10. 84)	4-8
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V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers..... because they relate to subject matter¹² not required to be searched by this Authority, namely:
2. ☐ Claim numbers..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹², specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.